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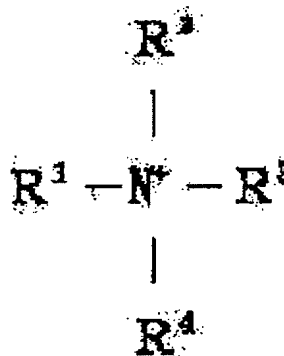
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## (54) ORGANIC CLAY COMPLEX CONTAINING MELAMINE RESIN AND AQUEOUS COATING MATERIAL COMPOSITION CONTAINING THE SAME

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain an organic clay complex containing a melamine resin aiming at the improvement of the dispersibility in an aqueous medium and the improvement in waterproofness of the obtained coated membrane by using the same as a viscosity increasing agent for an aqueous coating material by introducing a quaternary ammonium ion and a melamine resin between the layers of swelling layered silicic acid salt.

**SOLUTION:** This organic clay complex containing a melamine resin is obtained by introducing (B) a quaternary ammonium ion commonly available as an organic bentonite and expressed by formula I [R1 to R4 are each H, a 1-24C alkyl or an aralkyl, one of R1 to R4 is a ≥6C alkyl) between the layers of (A) a swelling layered silicic acid compound such as a natural or a synthesized smectite-based clay mineral, a swelling mica, a vermiculite, etc., having ≥10meq per 100g exchanging capacity and containing ≤30wt.% non clay impurities, by an ion exchange to obtain an organic clay complex material, then swelling the complex by contacting with an organic solvent and again introducing (C) a hydrophobic melamine resin soluble to an organic solvent, preferably having ≥1 triazine rings, and dissolved in the organic solvent.



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## CLAIMS

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[Claim(s)]

[Claim 1]A melamine resin content organic clay complex in which melamine resin of fusibility was introduced into the 4th class ammonium ion and an organic solvent between layers of a swelling laminar silicate.

[Claim 2]The melamine resin content organic clay complex according to claim 1 in which said melamine resin is hydrophobicity.

[Claim 3]A water-soluble or water-dispersion acrylic resin, an alkyd resin, Film formation nature resin chosen from a group which consists of polyester resin and urethane resin at least one; a distemper constituent which contains according to claim 1 0.5 to 20% of the weight of melamine resin content organic clay complex; on the basis of water; and solid content.

[Claim 4]The distemper constituent according to claim 3 which contains further at least one sort of cross linking agents chosen from a group which consists of amino resin, block isocyanate, an epoxy resin, and phenol resin.

[Claim 5]The distemper constituent according to claim 3 which contains photoluminescent pigment further.

[Claim 6]a) A process of introducing the 4th class ammonium ion by ionic exchange between layers of a swelling laminar silicate, and obtaining an organic clay complex;

b) A manufacturing method of a melamine resin content organic clay complex which includes process; which contacts melamine resin which dissolved in an organic solvent to an organic clay complex swollen by process; which contacts this organic clay complex to an organic solvent, and swells it, and c organic solvent.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the distemper constituent containing a melamine resin content organic clay complex and it useful as a thickener for distemper constituents.

[0002]

[Description of the Prior Art]A two-layer silica tetrahedral layer has the sandwiched type three-tiered structure which sandwiched the magnesium octahedral layer or the aluminum octahedral layer in between, and, as for a typical laminar silicate mineral, this (several layers - tens of layers) is laminated.

[0003]The silicate layer of a swelling laminar silicate has negative charge, and this is usually neutralized by the alkali metal cation and alkaline-earth-metals cation which exist between layers. Between layers spreads easily, and SUKUME tightness system clay and swelling mica which are kinds of a swelling laminar silicate form the sol which distributes underwater and has thixotropy, and show viscous regulation ability.

[0004]However, if this is used as a thickener for distemper constituents as it is, by coagglutination with aqueous resin, it will be easy to start a maldistribution and viscous regulation ability will not be revealed. The water resisting property of a coat is reduced remarkably.

[0005]The swelling laminar silicate has cation-exchange ability, and forms an organic clay complex by making it react to various cationic organic compounds. For example, the organic clay complex which contains in JP,7-187657,A the 4th class ammonium ion which has a polyoxyethylene group, and the 4th class ammonium ion which has a polyoxypropylene group is indicated. This organic clay complex shows dispersibility to the organic solvent of comparatively high polarity, and it can be used for it as a thickener of a solvent system coating composition.

[0006]However, when the organic clay complex of an indication here is inferior to the dispersibility in the inside of an aqueous medium and it is used as a thickener of distemper, it has the problem that the water resisting property of the coat obtained is inferior.

[0007]

[Problem(s) to be Solved by the Invention]There is a place which this invention solves the above-mentioned conventional problem, and is made into the purpose in providing the melamine resin content organic clay complex which does not degrade the water resisting property of the coat obtained, when it excels in the dispersibility in the inside of an aqueous medium and is used as a thickener of distemper.

[0008]In this specification, the "aqueous medium" refers to the mixture of the organic solvent which can be mixed with water, and water and water.

[0009]

[Means for Solving the Problem]This invention provides a melamine resin content organic clay complex in which melamine resin of fusibility was introduced into the 4th class ammonium ion and an organic solvent between layers of a swelling laminar silicate, and the above-mentioned purpose is attained by that.

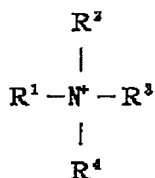
[0010]

[Embodiment of the Invention]The argillite of nature or a compounded smectite system, swelling mica, BAMYU curite, etc. are contained in the swelling laminar silicate used by this invention. Hectorite, saponite, a SUCHIBUN site, montmorillonite, bentonite, etc. are mentioned as the example of a natural smectite. As synthetic smectite, what is shown by formula  $\text{Na}_{0.1-1.0}\text{Mg}_{2.4-2.9}\text{Li}_{0.1-0.6}\text{Si}_{3.5-4.0}\text{O}_{9.0-10.6}(\text{OH and/or F})_{1.5-2.5}$  is mentioned. This is compounded by the method of a statement by the 0014-0019th paragraphs of JP,7-187657,A. As swelling mica used by this invention, what is compounded by the method of a statement is mentioned to the 0020th paragraph of JP,7-187657,A.

[0011]A swelling laminar silicate desirable although it is used by this invention has 10 or more milliequivalent per 100g of ionic exchange equivalents of 60 or more milliequivalent preferably. Generally, nature and synthetic SUKUME tightness have the ionic exchange equivalent of 85 to 130 milliequivalent per 100g. As for the quantity of a non-clay impurity, although a swelling laminar silicate may contain 50 or less % of the weight of a non-clay impurity, it is preferred that it is 30 or less % of the weight.

[0012]The 4th class ammonium ion used by this invention has a long-chain alkyl group, and is usually used for the organic clay complex marketed as organic bentonite.

[0013]The desirable 4th class ammonium ion is a formula. [Formula 1]



It is a compound come out of and shown. Among a formula, independently, although  $R^1 - R^4$  are the alkyl groups or aralkyl groups to a hydrogen atom or the carbon number 24, here, respectively, As for at least one of  $R^1 - R^4$ , when the 4th class ammonium ion takes expanding between layers into consideration, it is preferred that it is a with a carbon numbers of six or more alkyl group. When the water resisting property of the coat produced by using the melamine resin content organic clay complex of this invention for distemper is taken into consideration, as for  $R^1 - R^4$ , it is preferred respectively that it is the alkyl group or aralkyl group of the carbon numbers 6-24 independently, and it is still more preferred that it is an alkyl group of the carbon numbers 8-24. Generally that in which the carbon number of  $R^1 - R^4$  exceeds 24 is difficult to receive.

[0014] A methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, benzyl, an octyl group, a nonyl group, a decyl group, dodecyl, a pentadecyl group, an octadecyl group, etc. are mentioned as an example of  $R^1 - R^4$ .

[0015] Especially if melamine resin used by this invention is a thing of fusibility, it will not be limited to an organic solvent. Since insoluble melamine resin is inferior to an organic solvent at compatibility with an organic clay complex, it is not desirable. It is hydrophobicity and melamine resin which has at least one triazine ring in intramolecular is still more preferred.

[0016] As an example of desirable melamine resin, methoxy methylolmelamine, n-butoxymethylolmelamine, isobutoxymethylolmelamine, methoxy butoxymethylolmelamine, those condensates, etc. can be mentioned to alkoxy methylolmelamine and a concrete target. Although a desirable thing is methoxy methylolmelamine of the average condensation degrees 1-4, or n-butoxymethylolmelamine, if it is melamine resin which has at least one triazine ring, it will not be limited in particular.

[0017] A melamine resin content organic clay complex of this invention, First, introduce the 4th class ammonium ion by ionic exchange between layers of a swelling laminar silicate, obtain an organic clay complex, contact this organic clay complex to an organic solvent, make it swell it, and subsequently, It is obtained by contacting melamine resin which dissolved in an organic solvent to an organic clay complex swollen by an organic solvent.

[0018] An organic clay complex can be prepared by various ways were known by person skilled in the art. For example, a method of a statement is mentioned [ column / 8th / of 2-21st line / of JP, 7-187657, A ]. Generally, since preparation of an organic clay complex is performed in an aqueous medium, an organic clay complex obtained also usually contains an aqueous medium.

[0019] If an organic clay complex containing this aqueous medium is contacted to an organic solvent by being immersed into an organic solvent, for example, it will absorb this and will swell further. Thus, if an organic clay complex which swelled by an organic solvent is contacted to melamine resin which dissolved in an organic solvent, it will incorporate melamine resin between layers. Although a constant rate of aqueous media may be emitted from an organic clay complex in that case, water emitted in that case is removed.

[0020] melamine resin — a weight ratio of an organic clay complex and melamine resin — 5:1-1:5 — it is preferably added in 3:1-1:3, and quantity set to 2:1-1:2 still more preferably. When an addition of melamine resin was less than the weight ratio 5:1 of an organic clay complex and melamine resin and it uses as a thickener for distemper constituents, the dispersibility of a thickener in inside of a paint is checked. When it exceeded 1:5 and uses as a thickener of a distemper constituent, viscous regulation ability to expect is not revealed.

[0021] Since an alkyl chain within between layers and affinity of melamine resin are high, a reason melamine resin is incorporated between layers of an organic clay complex which swelled by an

organic solvent is considered.

[0022]A process which contacts an organic clay complex to an organic solvent, and a process contacted to melamine resin which dissolved in an organic solvent may be performed in one step. In that case, direct contact is carried out to melamine resin which dissolved an organic clay complex in an organic solvent.

[0023]As for an organic solvent which swells an organic clay complex, what has compatibility in either the 4th class ammonium ion and melamine resin is preferred. The kind will not be asked, if it has such character and existence is permitted in a distemper constituent. Specifically Aromatic systems, such as toluene and xylene, ethanol, isopropyl alcohol, A thing of petroleum systems, such as ester systems, such as ketone systems, such as an alcohol system of butanol etc., acetone, methyl isobutyl ketone, and methyl ethyl ketone, ethyl acetate, and butyl acetate, PETORORIUMU naphtha, and a mineral spirit, other cellosolve systems, and a carbitol system, etc. are mentioned.

[0024]As for a solvent in which melamine resin is dissolved, what has compatibility in melamine resin to be used is preferred. What an organic solvent which swells an organic clay complex specifically mentioned by the way can be used.

[0025]Although a reaction advances enough at a room temperature, it may be heated. A maximum temperature of heating is governed by the heat resistance of an organic clay complex to be used, and if it is below the decomposition point, it can be set up arbitrarily. A melamine resin organic clay complex obtained is a gel semisolid. This accepts necessity, and is dried and ground.

[0026]A melamine resin content organic clay complex contains an organic clay complex in 67 to 33% of the weight of quantity still more preferably 75 to 25% of the weight preferably 83 to 17% of the weight on the basis of solid content. When content of an organic clay complex was less than 17 % of the weight and it uses as a thickener of a distemper constituent, viscous regulation ability to expect is not revealed. If it exceeds 83 % of the weight, the dispersibility of a thickener in inside of a paint will be checked, and viscous regulation ability will fall, and an appearance-of-film fall and a waterproof fall will be produced.

[0027]A melamine resin content organic clay complex contains melamine resin in 33 to 67% of the weight of quantity still more preferably 25 to 75% of the weight preferably 17 to 83% of the weight on the basis of solid content. When content of melamine resin was less than 17 % of the weight and it uses as a thickener of a distemper constituent, viscous regulation ability to expect is not revealed. If it exceeds 83 % of the weight, the dispersibility of a thickener in inside of a paint will be checked, and viscous regulation ability will fall, and an appearance-of-film fall and a waterproof fall will be produced.

[0028]A melamine resin content organic clay complex of this invention can be used as a thickener or a gelling agent as it is. Generally, a thickening effect is so high that there are many additions.

[0029]A melamine resin content organic clay complex of this invention, In order to show thickening and the gelling effect excellent in a little addition, in required water cosmetics, drugs, a health agent, adhesives, a paint, and a painting material, viscous adjustment can use as constituents, such as a viscosity modifier, a dispersing agent, an emulsifier, and a binder, and is very useful. Furthermore, since this melamine resin content organic clay complex contains the 4th class ammonium ion, it can be used also as a spray for preventing static electricity of a plastic or textiles, a germicide, a dyeing assistant, a level dyeing agent, and a coupling agent. It can also use using the sheaf space as an organic substance conservative, a \*\*\*\* agent, a catalyst, a separating medium, adsorbent, resin stabilizer, a polymerization initiator, a carrier, a filler, etc.

[0030]A melamine resin content organic clay complex of this invention is suitable especially to adjust viscosity of a distemper constituent containing water-soluble or water-dispersion film formation nature resin. It is because the water resisting property of a coat obtained does not deteriorate even if it makes a distemper constituent contain a melamine resin content organic clay complex of this invention.

[0031]That is, according to this invention, water-soluble or water-dispersion film formation

nature resin, water, and a distemper constituent containing an above-mentioned melamine resin content organic clay complex are provided. A distemper constituent of this invention may contain a cross linking agent and various additive agents if needed.

[0032]Content of a melamine resin content organic clay complex is two to 10 weight section still more preferably one to 15 weight section preferably 0.5 to 20 weight section in solid content conversion to film formation solid content 100 weight section contained in a distemper constituent. When content of a melamine resin content organic clay complex is less than 0.5 weight sections, there is a possibility that viscous regulation ability to expect may not be revealed. Even if it exceeds and adds 20 weight sections, since there is no change in viscosity obtained, it is not economical. Although "film formation solid content" as used herein means solid content of water-soluble or water-dispersion film formation resin, when a hardening agent is included if needed, the sum with solid content of film formation resin of solid content of a hardening agent, water solubility, or water dispersibility is meant.

[0033]As water-soluble or water-dispersion film formation nature resin, an acrylic resin, polyester resin, alkyd resin, polyurethane resin, etc. can be mentioned, for example. These can use together one sort or two sorts or more.

[0034]As the above-mentioned acrylic resin, for example A carboxyl group containing vinyl monomer (M-1), A neutralized substance etc. of the acid value 10 [ about ] - the about 150 hydroxyl value 20 [ about ] - the about 200 number average molecular weight 3000 [ about ] which are produced by carrying out copolymerization of a hydroxyl group content vinyl monomer (M-2) and the other vinyl monomers (M-3) - about 100000 acrylic resin can be mentioned. When it is hard to dissolve the above-mentioned acid value in water by less than about ten and it exceeds about 150, coat performance may fall under influence of a residual carboxyl group.

[0035]The above-mentioned carboxyl group vinyl monomer (M-1) is a compound which has one or more carboxyl groups and one polymerization nature unsaturated bond in one molecule, and acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, etc. are mentioned, for example.

[0036]The above-mentioned hydroxyl group content vinyl monomer (M-2) is a compound which has a hydroxyl group and one polymerization nature unsaturated bond in one molecule, respectively, and this hydroxyl group acts as a functional group which mainly reacts to a cross linking agent. As such a thing, a monoester ghost of acrylic acid or methacrylic acid, and dihydric alcohol of 2-10 carbon numbers is preferred, For example, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, etc. can be mentioned.

[0037]It is a compound which the above and other vinyl monomers (M-3) are things other than both the above-mentioned monomers, and has one polymerization nature unsaturated bond in one molecule, For example, methyl acrylate, methyl methacrylate, ethyl acrylate, Ethyl methacrylate, propylacrylate, propyl methacrylate, Butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, cyclohexyl acrylate, A monoester ghost of acrylic acid, such as cyclohexyl methacrylate, laurylacrylate, and RAARIRU methacrylate, or methacrylic acid, and monohydric alcohol of the carbon numbers 1-20; Styrene, Aromatic system vinyl monomers, such as alpha-methylstyrene and vinyltoluene; Glycidyl acrylate, Glycidyl group content vinyl monomers, such as glycidyl methacrylate; Dimethylamino ethyl acrylate, Nitrogen-containing alkyl (carbon numbers 1-20) (meta) KURIRETO, such as dimethylamino methacrylate; Acrylic acid amide, An methacrylic acid amide, dimethylacrylamide, N,N-dimethylpropylacrylamide, N-butoxy methylacrylamide, N-methylolacrylamide, Polymerization nature unsaturated bond content amide system compounds, such as N-methylolmethacrylamide and diacetone acrylamide; VCM/PVC, Polymerization nature unsaturated bond content nitrile system compounds, such as vinyl compound; acrylonitrile, such as vinyl acetate and vinyl propionate, and a methacrylonitrile; diene series, such as butadiene and isoprene, etc. can be mentioned. The above and other vinyl monomers (M-3) can use one sort or two sorts or more.

[0038]A copolymerization reaction of the above-mentioned vinyl monomer can be performed by a publicly known method. An acrylic resin obtained can be used for water soluble acrylic resin, and nothing and this invention by neutralizing by monoamine.

[0039]The above-mentioned acrylic resin can be used for particle-like water dispersion acrylic resin with a mean particle diameter of 0.05–5.0 micrometers, and nothing and this invention by carrying out an emulsion polymerization under existence of dispersion stabilizer like a surface-active agent. As for the above-mentioned vinyl monomer which carries out an emulsion polymerization, what was chosen from the above-mentioned monomer (M-1), a monomer (M-2), and a monomer (M-3) is preferred. Since water dispersion acrylic resin which constructed the bridge in a grain child who uses together a little multi-vinyl compounds (M-4) which furthermore have a polymerization nature unsaturated bond in [ two or more ] one molecule if needed is obtained and coat performance improves further, it is desirable.

[0040]As the above-mentioned multi-vinyl compound (M-4), for example Ethylene glycol diacrylate, Ethylene glycol dimethacrylate, triethylene glycol diacrylate, tetraethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, divinylbenzene, trimethylolpropane triacrylate, etc. can be mentioned.

[0041]What neutralized the above-mentioned water dispersion acrylic resin by monoamine can be used for this invention.

[0042]A multilayer-structure emulsion called a core / shell type as the above-mentioned water dispersion acrylic resin is also useful. The above-mentioned emulsion is a water dispersing element by which acrylic resin particles currently distributed underwater are stabilized by stabilizer polymer, and this is an emulsion of the core / shell type which makes the above-mentioned acrylic resin particles a core part and with which it makes stabilizer polymer a shell part. The emulsion polymerization of the vinyl monomer component which completely or hardly contains a carboxyl group containing vinyl monomer (M-1) first is specifically carried out, Then, since this thing obtained by adding and carrying out the emulsion polymerization of the vinyl monomer component which contained a carboxyl group containing vinyl monomer (M-1) so much is thickened by neutralizing using monoamine, it is preferred also from a coating operability field.

[0043]Water dispersibility urethane resin used by this invention, (a) Aliphatic series or alicyclic polyisocyanate, (b) polymer polyol, (c) alpha and alpha-dimethylolmonocarboxylic acid, (d) chain extension agent, and a terminator on the other hand, Use (e)1 class and the 2nd class monoamine as an ingredient, and under existence of an organic solvent or nonexistence And the above (a), (b) And make the (d) ingredient react by one-shot process or a multi stage method, and make carboxyl group content polyurethane resin form by the (c) ingredient and necessity, (e) It is the aqueous dispersion of self-emulsification type polyurethane resin with a mean particle diameter of about 0.001–3.0 micrometers prepared by mixing with water and distilling off a solvent by a dispersing element, nothing, and necessity, neutralizing a neutralization rear stirrup of an ingredient.

[0044]Aliphatic series or alicyclic polyisocyanate of the above-mentioned (a) ingredient, With a compound which has two or more isocyanate groups, aliphatic carbon groups, or alicyclic carbon groups in one molecule. For example, hexamethylene di-isocyanate (HDI), 2,2,4-trimethylhexane diisocyanate, Aliphatic series diisocyanate of the carbon numbers 2–12, such as lysine diisocyanate; 1,4-cyclohexane diisocyanate (CDI), Isophorone diisocyanate (IPDI), 4, and 4'-dicyclohexylmethane diisocyanate (hydrogenation MDI), Methylcyclohexane diisocyanate, the isopropylidene dicyclohexyl 4, 4'-diisocyanate, Cycloaliphatic diisocyanate of the carbon numbers 4–18, such as a 1,3-diisocyanatomethylcyclohexane (hydrogenation XDI); Xylylene diisocyanate (XDI), Aliphatic series diisocyanate which has aromatic rings, such as tetramethyl xylylene diisocyanate (TMXDI); Carbodiimide, A denaturation thing of the above-mentioned diisocyanate, such as URECHI dione, URETO imine, view let and an isocyanurate denaturation thing, and an isocyanurate denaturation thing; two or more sorts of mixtures of these, etc. are mentioned. HDI, IPDI, and the hydrogenation MDI and TMXDI are [ among these ] preferred. (a) If aromatic polyisocyanate is used as an ingredient, since a coat will turn yellow easily at the time of baking hardening and it will be easy to discolor a coat under the influence of ultraviolet rays, it is not desirable.

[0045]As polymer polyol of the above-mentioned (b) ingredient, On the other hand, heterocyclic ether, such as alkylene oxide, such as ethylene oxide, propylene oxide, and butylene oxide, and a tetrahydrofuran, or a thing which can obtain both sides by polymerizing or carrying out

copolymerization, For example, a polyethylene glycol, a polypropylene glycol, polyethylene polypropylene (block or random) glycol, Polyethylene tetramethylene glycol (a block or random), Polytetramethylene ether glycol, polyhexamethylene ether glycol, etc.; Polyester polyol, for example, aliphatic dicarboxylic acid (succinic acid, adipic acid, sebacic acid, and glutaric acid.) low molecule glycol (ethylene glycol.) with aromatic dicarboxylic acid (isophthalic acid, terephthalic acid, etc.), such as azelaic acid Propylene glycol, 1,4-butanediol, 1,6-hexanediol, That to which condensation polymerization of 3-methyl-1,5-pentanediol, neopentyl glycol, the 1,4-dihydroxymethylcyclohexane, etc. was carried out, for example, polyethylene adipate diol, polybutylene adipate diol, polyhexamethylene adipate diol, Polyneopentyl adipate diol, polyethylene / butylene horse mackerel peat diol, Poly 3-methylpentane AJIPETO diol, polybutylene isophthalate diol, etc.; Polylactone polyol, For example, polycaprolactone diol or triol, Poly 3-methylvalerolactonediol, etc.; Polycarbonatediol, For example, polyhexamethylene carbonate diol;; two or more sorts of these mixtures, etc., such as polyolefine polyol, for example, polybutadiene glycol, or its hydride, can be mentioned.

[0046]Desirable things are polyester polyol, polylactone polyol, polycarbonate polyols and these mixtures, or a mixture of these and polyether polyol among the above-mentioned polymer polyol. As for a molecular weight of polymer polyol, 500-5000 are preferred, and 1000-3000 are more preferred.

[0047]It is an ingredient used in order that alpha of the above-mentioned (c) ingredient and alpha-dimethylolmonocarboxylic acid may introduce an anionic hydrophilic group for making polyurethane resin distribute underwater stably. As an example, alpha and alpha-dimethylolacetic acid, alpha, and alpha-dimethylol-propionic-acid, alpha, and alpha-dimethylolbutanoic acid etc. are mentioned, and a desirable thing is alpha and alpha-dimethylol propionic acid. As for quantity of alpha and alpha-dimethylolmonocarboxylic acid, 0.3 to 5 % of the weight is preferred among urethane resin which reacts above-mentioned (a) - (c) ingredient as a carboxyl group, and its 0.5 to 3 % of the weight is more preferred. At less than 0.3 % of the weight, since the hydrophilic nature of polymer will become high if it is hard to obtain a stable emulsion and exceeds 5 % of the weight, there is a possibility that an emulsion may serve as hyperviscosity and the water resisting property of a coat may fail.

[0048]A chain extension agent and a terminator of the above-mentioned (d) ingredient may be used as occasion demands when manufacturing a urethane resin emulsion. Low molecule polyol and polyamine are mentioned as a chain extension agent. Glycol mentioned as a raw material of the above-mentioned polyester polyol as the above-mentioned low molecule polyol, for example, and an alkylene oxide low mol addition of the alkylene oxide low mol addition (less than 500 molecular weight); bisphenol (less than 500 molecular weight); Trihydric alcohol, For example, alkylene oxide low mol addition (less than 500 molecular weight); and two or more sorts of these mixtures, such as glycerin, trimethyloethane, and trimethylolpropane, are mentioned. As the above-mentioned polyamine aliphatic polyamine, for example, ethylenediamine, N-hydroxyethyl ethylenediamine, a tetramethylenediamine, Hexamethylenediamine, diethylenetriamine, etc.; Alicycle fellows polyamine, For example, 4,4'-diaminohexylmethane, 1,4-diaminocyclohexane, Isophoronediamine etc.; Aliphatic polyamine which has an aromatic ring. For example, xylylene diamine, tetramethyl xylylene diamine, etc.;; and two or more sorts of these mixtures, such as aromatic polyamine, for example, 4,4'-diaminodiphenylmethane, tolylenediamine, benzidine, and a phenylenediamine, are mentioned.

[0049]As for loadings of the above-mentioned chain extension agent, 0.3 to 30 % of the weight is preferred to polymer polyol of the above-mentioned (b) ingredient, and its 0.5 to 20 % of the weight is more preferred.

[0050]As a terminator, low molecule monoalcohol, univalent alkylamine (methanol, butanol, cyclohexanol, etc.) (mono- and di-ethylamine, mono-, a di-butylamine, etc.), alkanolamines (mono-, di-ethanolamine, etc.), etc. are mentioned.

[0051]As the 1st class and the 2nd class monoamine of the above-mentioned (e) ingredient which are used for neutralization of a carboxyl group, Ammonia; Low-grade alkylamine, for example, methylamine, ethylamine, Isopropylamine, n-butylamine, dimethylamine, diethylamine, Diisopropylamine, di-n-butylamine, etc.; Alicycle fellows amine. For example, cyclohexylamine

etc.; Heterocyclic amine, for example, morpholine, Pyridine etc.; and two or more sorts of these mixtures, such as alkanolamine, for example, monoethanolamine, diethanolamine, monoisopropanolamine, diisopropanolamine, methylethanol amine, and methyliso propanolamine, are mentioned. A thing desirable [ among these ] is the alkanolamine of the 2nd class.

[0052]As for the amount of monoamine used, 0.5–1.5 Eq is preferred to 1.0 Eq of carboxyl groups, and its 0.7–1.3 Eq is more preferred.

[0053]The 1st class and the 2nd class monoamine are useful also as a neutralizer of the above-mentioned water solubility or water dispersion acryl resin.

[0054]As for the above-mentioned polyurethane resin formation reaction, 20–150 \*\* is preferred, and its 50–120 \*\* is more preferred. However, when making amine react, 80 \*\* or less is preferred and 0–70 \*\* is more preferred. In order to promote a reaction, a catalyst of an amine system used for the usual urethane-ized reaction or a tin system may be used. When using a solvent, especially a thing that has water and the boiling point below comparable by water solubility is preferred.

[0055]Polyester resin used by this invention can be obtained by a polycondensation reaction of polybasic acid and polyhydric alcohol. It is not limited especially as such polybasic acid, but For example, oxalic acid, succinic acid, Straight chain dibasic acid, such as a succinic anhydride, adipic acid, azelaic acid, and sebacic acid; Phthalic acid, Phthalic anhydride, isophthalic acid, terephthalic acid, tetrahydro phthalic anhydride, Hexahydrophthalic acid, hexahydro phthalic anhydride, tetra bromine phthalic anhydride, Aromatic fatty acid, such as trimellitic acid, trimellitic anhydride, pyromellitic acid, and pyromellitic dianhydride; unsaturation dibasic acid, such as maleic acid, a maleic anhydride, boletic acid, and itaconic acid, etc. can be mentioned.

[0056]It is not limited especially as such polyhydric alcohol, but For example, ethylene glycol, Propylene glycol, 1,3-butylenediol, 1,6-hexanediol, Glycols, such as a diethylene glycol, neopentyl glycol, and triethylene glycol; Hydrogenation bisphenol A, Bisphenol dihydroxypropyl ether, glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, etc. can be mentioned.

[0057]In addition to the above-mentioned polybasic acid and the above-mentioned polyhydric alcohol, a monobasic acid or monohydric alcohol can be suitably used for the above-mentioned polyester resin for the purpose of molecular weight regulation with a conventional method.

[0058]It can obtain the above-mentioned polyester by the ability of ester denaturation of the alkyd resin used by this invention to be carried out with drying oil, fatty acid, etc. As the above-mentioned drying oil and fatty acid, linseed oil, tung oil, oiticica oil, drying castor oil, palm oil, hydrogenation palm oil, U.S. sugar fatty acid, talloil fatty acid, soybean oil, octylic acid, etc. can be mentioned, for example. The above-mentioned alkyd resin may be a thing of epoxy denaturation, rosin denaturation, and phenol resin denaturation. These can be manufactured by a publicly known method.

[0059]A distemper constituent of this invention may contain a cross linking agent and various additive agents if needed, as stated previously.

[0060]It will not be limited, especially if it is the cross linking agent known by person skilled in the art noting that a bridge is constructed in a hydroxyl group or an acid radical which exists in distributed resin as a hardening agent. It is preferred to use at least one sort of an amino compound, an isocyanate compound, and an epoxy compound.

[0061]Specifically, they are blocking polyisocyanate and an alkoxy \*\* melamineformaldehyde condensate (it is an alkoxy ghost of a condensate with melamineformaldehyde or paraformaldehyde, and). For example, methoxy methylolmelamine, isobutoxy-ized methylolmelamine, An epoxy compound containing n-butoxy-ized methylolmelamine, butyl-ized melamine, and two epoxy groups or more. for example, ShellChemical "Epicoat 828" -- "the 1001". -- the 1004", the "EPO light 40E" by a \*\*\*\* fats-and-oils company, "said 400E", "the #1600", "the #721", and "DENAKORU EX-301" by Nagase Brothers Chemicals -- "the 622" -- "the 512" -- and -- "the 421" -- etc. -- it is mentioned, and these can be used, mixing.

[0062]In a distemper constituent of this invention, photoluminescent pigment, a color pigment, and an extender which are generally used to the usual distemper constituent can be added if needed.

[0063]As the above-mentioned photoluminescent pigment, a mica pigment etc. which consist of

metal paints or metallic oxides, such as an aluminum paints paste, are used. As the above-mentioned color pigment, organic system color pigments, such as inorganic system color pigments, such as red yellow paints, such as white pigments, such as a titanium dioxide, and iron oxide, SHINKASHA red, cyanine blue, and carbon black, are mentioned, for example. Clay, talc, etc. are mentioned as the above-mentioned extender. These are used as a distributed paste.

[0064]For improvement in the weatherability of a coat produced by paint of the above-mentioned distemper constituent, antioxidants, such as ultraviolet ray absorbents, such as a benzo phenol system, hindered amine light stabilizer, and a phenol system, etc. may be added. A surface control agent for adjustment of paint film appearance, such as a rheology control agent, may be blended as other addition ingredients.

[0065]A distemper constituent of this invention can be prepared by carrying out stirring mixing of each above-mentioned ingredient uniformly. An addition order of each above-mentioned ingredient, addition conditions in particular, etc. are not limited, but can be performed by a usual method.

[0066]The usual paint means, such as atomized spray painting, brush coating paint, dip coating, roll coating, and flow coating paint, can be used for paint of a distemper constituent of this invention.

[0067]Especially as a coated object, automobile shells, such as a passenger car, a bus, a truck, and a motorcycle, are preferred. It is not limited only to these. The above-mentioned coated object does not interfere, even if either made from metal and plastics is good and has painted a primer and an intermediate coat beforehand to metal coated objects.

[0068]A distemper constituent of this invention can be used very conveniently as base coating at the time of painting by the two quart 1 bake method. A distemper constituent of this invention so that it may become about 10-50-micrometer dry membrane thickness For example, an air spray, It paints to metal coated objects by airless spray, electrostatic coating, etc., it is made to dry until a volatile constituent will be about 15 or less % of the weight preferably 25 or less % of the weight by air-drying or warm air desiccation, and it paints by electrostatic coating etc. so that it may become about 15-70 micrometers of dry membrane thickness about a clear coating material on it. Next, 100-180 \*\* after performing the usual setting. For [ 15 to 30 minutes ] grade heating is more preferably carried out at about 120-160 \*\*, and it is considered as a cured film.

[0069]By such paint, a coat which was excellent in the very good water resisting property of appearance and adhesion can be obtained.

[0070]After degreasing a coated object if needed and performing primer paint etc. in paint to a coated object made from a plastic, it can paint like a case of the above-mentioned metal coated objects. In this case, when stiffening base coating and a clear coating material which were recoated, less than heat deflection temperature of a plastic carries out temperature.

[0071]As a clear coating material painted on a painted surface of the above-mentioned distemper constituent, a publicly known thing can be used from the former. As such a clear coating material, organic solvent dilution type paints, such as amino alkyd resin, an acrylic resin, an amino acrylic resin, amino oil free alkyd resin, silicon polyester resin, a fluoro-resin, and a urethane resin system, are mentioned, for example.

[0072]A granular material clear coating material which does not use an organic solvent can also be used.

[0073]A distemper constituent of this invention can also be independently painted, although it is preferred to use it as a base coating of the two quart 1 bake method.

[0074]

[Example]Although the following examples explain this invention still in detail, this invention is not limited to these. A "part" is a weight reference unless it refuses in particular.

[0075]76 copies of ethylene glycol monobutyl ether was taught to the reaction vessel of 1L provided with the manufacture nitrogen introducing pipe of the manufacture 1-(1) film-formation nature resin varnish of example of manufacture 1-distemper, the agitator, the temperature control machine, and the condenser tube. The monomer solution was separately adjusted by mixing 15 copies of styrene, 63 copies of methyl methacrylate, 48 copies of 2-vitro KISHIE chill

methacrylate, 117 copies of M-butyl acrylate, 27 copies of methacrylic acid, 30 copies of acrylamide, and three copies of azobisisobutyronitriles. 61 copies of this monomer solution was added to the reactor, and temperature was 120 \*\* under stirring. Subsequently, stirring was continued for 1 hour, after adding 245 copies of monomer solutions further over 3 hours. Then, 28 copies of dimethylethanolamines and 200 copies of deionized water were added, and the acrylic resin varnish of 50% of a nonvolatile matter, the number average molecular weight 12000 of resin, the OH value 70, and the acid value 58 was obtained.

[0076](2) the manufacture aluminum paints paste (a trade name "ARUPESUTO 7160N") of aluminum paints / melamine resin distribution paste 60 copies of melamine resin (a trade name "you van 20SB", butyl-ized melamine, 50% of a nonvolatile matter, the Mitsui Toatsu Chemicals make) was added and mixed homogenously to 65% of the aluminum content, and the Toyo Aluminium 15 copy. Furthermore two copies of isostearyl acid phosphate (a trade name "HOSUREKKUSU A-180L", the product made from the Sakai chemicals) was mixed homogenously, and aluminum pigment dispersion liquid was obtained.

[0077](3) 112 copies of film formation nature resin varnishes obtained by the manufacture stainless steel container of distemper by (1), and 77 copies of the aluminum pigment dispersion liquids / melamine resin distribution pastes which were obtained by (2) were taken, and distemper was manufactured by stirring with the agitator for an experiment.

[0078]80 copies of film formation nature resin varnishes obtained by the manufacture stainless steel container of the manufacture 2-(1) titanium oxide pigment / pitch powder paste for distemper of example of manufacture 2-distemper by (1) of the example 1 of manufacture are taken, With the agitator for an experiment, under stirring, 72 copies of deionized water carried out preliminary stirring, after adding 20 copies of titanium oxide pigments (a trade name "CR-97", the Ishihara Sangyo make) subsequently. Then, the two pass was carried out to the continuous system sealing horizontal-type dispersion machine (a "DYNO-MILL form KDL-PILOT type", the product made from Willy A Bachofen AG Maschinenfabrik), and the titanium oxide pigment dispersion paste was obtained.

[0079](2) 100 copies of the titanium oxide pigment / pitch powder pastes for distemper which were obtained by the manufacture stainless steel container of distemper by (1), Eight copies of melamine resin (a trade name "you van 20SB", butyl-ized melamine, 50% of a nonvolatile matter, the Mitsui Toatsu Chemicals make) was taken further, and 24 copies of film formation nature resin varnishes obtained by (1) of the example 1 of manufacture manufactured distemper by stirring with the agitator for an experiment.

[0080]The titanium oxide pigment / pitch powder paste 100 weight section for distemper obtained by the manufacture stainless steel container of the manufacture 3-(1) distemper of example of manufacture 3-distemper by (1) of the example 2 of manufacture, the film formation nature resin varnish obtained by (1) of the example 1 of manufacture --- distemper was manufactured by taking block isocyanate (trade name "coronate 2507", product made from Japanese polyurethane) 7.5 weight section further, and agitating with the agitator for an experiment 20 weight section.

[0081]Manufacture (1)-1 of the manufacture 4-(1) film-formation nature resin varnish of example of manufacture 4-distemper The synthesizing temperature meter of hydrophilic oligomer, Dimethylol-propionic-acid 40.2 weight section, triethylamine 30 weight section, and N-methyl-pyrrolidone 312 weight section were added to the 1000-ml reaction vessel provided with the agitator and the capacitor, and heating and dissolving were carried out to 90 \*\*. Next, isophorone diisocyanate 290 weight section and polypropylene-glycol (molecular weight: 1000) 700 weight section were added, and dibutyltin dilaurate 1.03 weight section was added after churning for 10 minutes. Next, temperature up was carried out and it was made to react to 95 \*\* for 1 hour.

(1)-2 The urethane prepolymer solution which added deionized water 1757 weight section and hydrazine hydrate 9.2 weight section to the 5000-ml reaction vessel provided with the temperature-of-adjustment meter of a water dispersing element, the agitator, the capacitor, and the dropping funnel, and was obtained by the above under churning was added. Then, churning was performed for 30 minutes. The obtained constituent was the stable water dispersing element

which became cloudy. The acid value of the solid content was 16.2, and the obtained nonvolatile matter was 33%.

(2) The titanium oxide pigment / pitch powder paste 100 weight section for distemper obtained by the manufacture stainless steel container of distemper by (1) of the example 2 of manufacture, the film formation nature resin varnish obtained by (1) — distemper was manufactured by taking melamine resin (trade name "you van 20SB", butyl-ized melamine, 50% of nonvolatile matter, Mitsui Toatsu Chemicals make) 8 weight section further, and agitating with the agitator for an experiment 37 weight section.

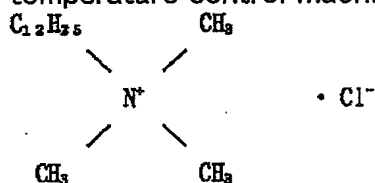
[0082] 70 copies of xylene and 20 copies of N-butanol were taught to the reaction vessel provided with the manufacture nitrogen introducing pipe, the agitator, temperature control machine, and condenser tube of manufacture—(1) varnish of an example of manufacture 5—clear coating material. The monomer solution was separately adjusted by mixing 1.2 copies of methacrylic acid, 26.4 copies of styrene, 26.4 copies of methyl methacrylate, 36.0 copies of N-butyl acrylate, 10.0 copies of 2-hydroxyethyl methacrylate, and 1.0 copy of azobisisobutyronitrile. It heated adding and stirring 20 copies of this monomer solution to a reaction vessel, and temperature was raised. Remaining 81.0 copies of a monomer solution were dropped over 2 hours, making it return, and the initiator solution which subsequently consists of 0.3 copy of azobisisobutyronitrile and ten copies of xylene was dropped over 30 minutes. Stirring flowing back of the reaction solution was carried out for further 2 hours, the reaction was ended, and the acrylic resin varnish of 50% of a nonvolatile matter, the number average molecular weight 8000, and the OH value 48 was obtained.

[0083] (2) To the reaction vessel of 2L provided with the manufacture nitrogen introducing pipe, the agitator, the temperature control machine, capacitor, and decanter of polyester resin. Temperature up of 134 copies of screw hydroxyethyl taurine, 130 copies of neopentyl glycol, 236 copies of azelain, 186 copies of phthalic anhydride, and 27 copies of xylene was taught and carried out. Azeotropy of the water generated by a reaction was carried out to xylene, and it was removed. Stirring and drying were continued until temperature was 190 \*\* over about 2 hours and the acid value of carboxylic acid was set to 145 from the flowing-back start, and then, it cooled to 140 \*\*. The temperature of 140 \*\* was held, the car Jura E10 (BASA tick acid glycidyl ester by shell company) 314 copy was dropped over 30 minutes, and the reaction was ended after continuing a reaction, stirring after that for 2 hours. The obtained polyester resin was the number average molecular weight 1054, the acid value 59, and the OH value 90.

[0084] (3) Ten copies of polyester resin and 0.75 copy of dimethylethanolamine which were manufactured by 282 copies of deionized water and (2) are taught, and it was made to dissolve in the reaction vessel of 1L provided with the manufacture nitrogen introducing pipe, the agitator, condensator, and temperature control machine of a resin particle, holding the bottom temperature of stirring at 80 \*\*. The initiator solution in which 45 copies of deionized water and 4.3 copies of dimethylethanolamines were made to dissolve 45 copies of azobis cyanovaleric acids was added here. Subsequently, the monomer solution which consists of 70.7 copies of methyl methacrylate, 94.2 copies of N-butyl acrylate, 70.7 copies of styrene, 30 copies of 2-hydroxyethyl acrylate, and 4.5 copies of ethylene glycol dimethacrylate was dropped at the reaction vessel over 1 hour. After dropping, the initiator solution which dissolved 1.5 copies of azobis cyanovaleric acids in 15 copies of deionized water and 1.4 copies of dimethylethanolamines was added, and it stirred at 80 \*\* for 1 hour. As a result, the with 45% of a nonvolatile matter, pH 7.2 viscosity of 92 cps (25 \*\*), and a particle diameter of 0.156 micrometer emulsion was obtained. By adding 200 copies of xylene to the resin particle which carried out spray drying of this emulsion, and was obtained except for water to 100 copies of resin particles, re dispersion was carried out and the xylene dispersing element of the resin particle was produced. Particle diameter was 0.3 micrometer.

[0085] (4) 100 copies of varnishes manufactured by (1) in the manufacture stainless steel container of the clear coating material, 2.2 copies of resin particles manufactured by you van 20SE-60 (butylated melamine resin by Mitsui Toatsu Chemicals, Inc.) 36 copy, 0.5 copy of MODAFURO (Monsanto Co. tabulation side regulator), and (3) were taken, and the clear coating material was manufactured by stirring with the agitator for an experiment.

[0086] It is a formula to the 1-l. reaction vessel provided with example 1 agitator, the temperature control machine, and the condenser tube. [Formula 2]



It came out, 7.6 copies of quarternary ammonium salt and 392.4 copies of ion exchange water which are shown were prepared and agitated, and it was made the temperature of 70 \*\*. 600 copies of water dispersions which consist of 12 copies of swelling laminar silicates (a trade name "KUNIPIAF", the product made from KUNIMINE) and 588 copies of ion exchange water were added maintaining at 70 \*\* of reaction vessel internal liquid, and churning was continued for 2 hours. After condensing the obtained water dispersion by centrifugal separation, 1000 copies of ion exchange water was added and washed. The water dispersion furthermore obtained was condensed by centrifugal separation. The solid content of the obtained slurry was 15 % of the weight.

[0087] 130 copies of slurries obtained by the stainless steel beaker were taken, and 39 copies of butylated melamine resin by the bottom of churning and Mitsui Toatsu Chemicals "you van 20SB", one copy of diethylene glycol monoethyl ether, and 49 copies of solutions that mixed nine copies of Solvesso 150 beforehand were added with the agitator for hyperviscosity. By furthermore agitating, 110.5 copies of water to which it was able to begin to come was removed, and the thickener for distemper was obtained from the slurry.

[0088] Example 2 melamine resin is changed into Mitsui Toatsu Chemicals methoxy-ized methylol melamine resin "Cymel 303". The thickener for distemper was obtained like Example 1 except using 26.55 copies of 19.5 copies of melamine resin, 2.95 copies of diethylene glycol monoethyl ether, and Solvesso 150.

[0089] The thickener for distemper was obtained like Example 2 except having changed example 3 melamine resin into Mitsui Toatsu Chemicals methoxy / butoxy mixing alkyl ether-ized methylol melamine resin "Cymel 235."

[0090] The thickener for distemper was obtained like Example 2 except having changed example 4 melamine resin into Mitsui Toatsu Chemicals butylated melamine resin "my coat 506."

[0091] 15.1 copies of thickeners for distemper obtained in Example 1 were added to 189 copies of distemper obtained in the example 1 of example 5 manufacture, and uniform dispersion was carried out to it with the agitator for an experiment. Ion exchange water was added so that the #4FC viscosity in 20 \*\* might be 30 seconds, and the distemper constituent was obtained.

[0092] The dispersibility of a distemper constituent and paint viscosity which were obtained were evaluated as follows.

[0093] Flow coating of the dispersibility 1. distemper constituent was carried out on the glass plate, and the existence of BUTSU and an aggregate was observed.

[0094] The three-stage level estimated dispersibility by the following standards. The obtained result is shown in Table 1.

[0095]

O; — \*\*\*\*\*, BUTSU and aggregate private seals, — BUTSU of certain quantity, and xwith aggregate; — a lot of BUTSU and those with an aggregate [0096] The viscosity of the distemper constituent was measured changing a shear rate at intervals of 1 minute using a paint viscosity E type viscosity meter (product made from TOKIMEC). The obtained result is shown in drawing 1.

[0097] Subsequently, the metal steel plate was degreased and the electrodeposition coat for cars and the middle-coat coat were provided on this. On this middle-coat coat, the distemper constituent prepared as mentioned above was applied so that it might become 12 micrometers of thickness, and predrying was carried out for 5 minutes at 60 \*\*. On the obtained coat, the oily clear coating material obtained in the example 3 of manufacture was applied so that it might

become 35 micrometers of thickness, and it printed for 20 minutes at 130 \*\*.

[0098]The water resisting property of the obtained laminating paint film was evaluated as follows.

[0099]The constant temperature bath with a water resisting property of 40 \*\* of the coat was made to immerse a laminating paint film board 3/4 times, and secondary adhesion was observed ten days afterward.

[0100]The three-stage level estimated the water resisting property by the following standards. A result is shown in Table 1.

[0101]

O; exfoliation [ in / in exfoliation / in / in the exfoliation in the secondary adherence test of a flood part / the secondary adherence test of a 0%\*\*; flood part / the secondary adherence test of a 1 to 50%x; flood part ] is 51 to 100%. [0102]The distemper constituent and the laminating paint film were obtained and evaluated like Example 5 except having changed the thickener for example 6 distemper into what was obtained in Example 2. A result is shown in Table 1 and drawing 2.

[0103]The distemper constituent and the laminating paint film were obtained and evaluated like Example 5 except having changed the thickener for example 7 distemper into what was obtained in Example 3. A result is shown in Table 1 and drawing 3.

[0104]The distemper constituent and the laminating paint film were obtained and evaluated like Example 5 except having changed the thickener for example 8 distemper into what was obtained in Example 4. A result is shown in Table 1 and drawing 4.

[0105]Seven copies of thickeners for distemper obtained in Example 1 were added to 132 copies of distemper obtained in the example 2 of example 9 manufacture, and uniform dispersion was carried out to it with the agitator for an experiment. Ion exchange water was added so that the #4FC viscosity in 20 \*\* might be 30 seconds, and the distemper constituent was obtained. The dispersibility of a distemper constituent and paint viscosity which were obtained were evaluated like Example 5.

[0106]Subsequently, except applying a distemper constituent so that it may become 35 micrometers of thickness, and not applying a clear coating material on it, the laminating paint film was obtained like Example 5, and the water resisting property was evaluated. A result is shown in Table 1 and drawing 5.

[0107]Thickener 7 weight section for distemper obtained in Example 1 by distemper 127.5 weight section obtained in the example 3 of example 10 manufacture was added, and uniform dispersion was carried out with the agitator for an experiment. Ion exchange water was added so that the #4FC viscosity in 20 more \*\* might be 30 seconds, and the distemper constituent was obtained. The dispersibility of a distemper constituent and paint viscosity which were obtained were evaluated like Example 5. Subsequently, except applying a distemper constituent so that it may become 35 micrometers of film pressure, and not applying a clear coating material on it, the laminating paint film was obtained like Example 5, and the water resisting property was evaluated. A result is shown in Table 1 and drawing 6.

[0108]Thickener 7 weight section for distemper obtained in Example 1 by distemper constituent 145 weight section obtained in the example 4 of example 11 manufacture was added, and uniform dispersion was carried out with the agitator for an experiment. Ion exchange water was added so that the #4FC viscosity in 20 \*\* might be 30 seconds, and the distemper constituent was obtained. The dispersibility of a distemper constituent and paint viscosity which were obtained were evaluated like Example 5. Subsequently, except applying a distemper constituent so that it may become 35 micrometers of film pressure, and not applying a clear coating material on it, the laminating paint film was obtained like Example 5, and waterproof evaluation was carried out. The result is shown in Table 1 and drawing 7.

[0109]Three copies of swelling laminar silicates (a trade name "KUNIPIAF", the product made from KUNIMINE) were added to 189 copies of distemper obtained in the example 1 of comparative example 1 manufacture, and uniform dispersion was carried out with the agitator for an experiment. Ion exchange water was added so that the #4FC viscosity in 20 \*\* might be 30 seconds, and the distemper constituent was obtained. The dispersibility of a distemper

constituent and paint viscosity which were obtained were evaluated like Example 5. Condensation of the thickener for distemper did not perform measurement of viscosity. [0110]Subsequently, the laminating paint film was obtained like Example 5, and the water resisting property was evaluated. A result is shown in Table 1.

[0111]Ion exchange water was added so that the #4FC viscosity in 20 \*\* might become the distemper obtained in the example 1 of comparative example 2 manufacture with 30 seconds, and the distemper constituent was obtained. The dispersibility of a distemper constituent and paint viscosity which were obtained were evaluated like Example 5.

[0112]Subsequently, the laminating paint film was obtained like Example 5, and the water resisting property was evaluated. A result is shown in Table 1 and drawing 1 - 4 as an object.

[0113]Ion exchange water was added so that the #4FC viscosity in 20 \*\* might become the distemper obtained in the example 2 of comparative example 3 manufacture with 30 seconds, and the distemper constituent was obtained. The dispersibility of a distemper constituent and paint viscosity which were obtained were evaluated like Example 5.

[0114]Subsequently, except applying a distemper constituent so that it may become 35 micrometers of thickness, and not applying a clear coating material on it, the laminating paint film was obtained like Example 5, and the water resisting property was evaluated. A result is shown in Table 1 and drawing 5.

[0115]The distemper constituent and the laminating paint film were obtained and evaluated like the comparative example 3 except having changed comparative example 4 distemper into what was obtained in the example 3 of manufacture. A result is shown in Table 1 and drawing 6.

[0116]The distemper constituent and the laminating paint film were obtained and evaluated like the comparative example 3 except having changed comparative example 5 distemper into what was obtained in the example 4 of manufacture. A result is shown in Table 1 and drawing 7.

[0117]

[Table 1]

Example No. Distemper Thickener Clear coating . Dispersibility Example of waterproof 5

manufacture 1 example 1 The example 5 of manufacture. O Example of O6 manufacture 1 example 2 The example 5 of manufacture. O Example of O7 manufacture 1 example 3 The example 5 of manufacture. O Example of O8 manufacture 1 example 4 The example 5 of manufacture. O Example of O9 manufacture 2 Example 1 - O O10. Example of manufacture 3 Example 1 Example of - O O11 manufacture 4 Example 1 Example of example of -O O comparison 1 manufacture 1 KUNIPIA F manufacture 5 x x comparison 2 Example 1 of manufacture Example of - manufacture 5 O O comparison 3 Example 2 of manufacture - - O O comparison 4 Example 3 of manufacture - - O O comparison 5 Example 4 of manufacture - - O O [0118]

[Effect of the Invention]When it excelled in the dispersibility in the inside of an aqueous medium and was used as a thickener of distemper, the melamine resin content organic clay complex which does not degrade the water resisting property of the coat obtained was provided.

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[Translation done.]

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- 3.In the drawings, any words are not translated.

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#### DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is viscosity change by the share of a distemper constituent (Example 5, the comparative example 2).

[Drawing 2] It is viscosity change by the share of a distemper constituent (Example 6, the comparative example 2).

[Drawing 3] It is viscosity change by the share of a distemper constituent (Example 7, the comparative example 2).

[Drawing 4] It is viscosity change by the share of a distemper constituent (Example 8, the comparative example 2).

[Drawing 5] It is viscosity change by the share of a distemper constituent (Example 9, the comparative example 3).

[Drawing 6] It is viscosity change by the share of a distemper constituent (Example 10, the comparative example 4).

[Drawing 7] It is viscosity change by the share of a distemper constituent (Example 11, the comparative example 5).

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[Translation done.]

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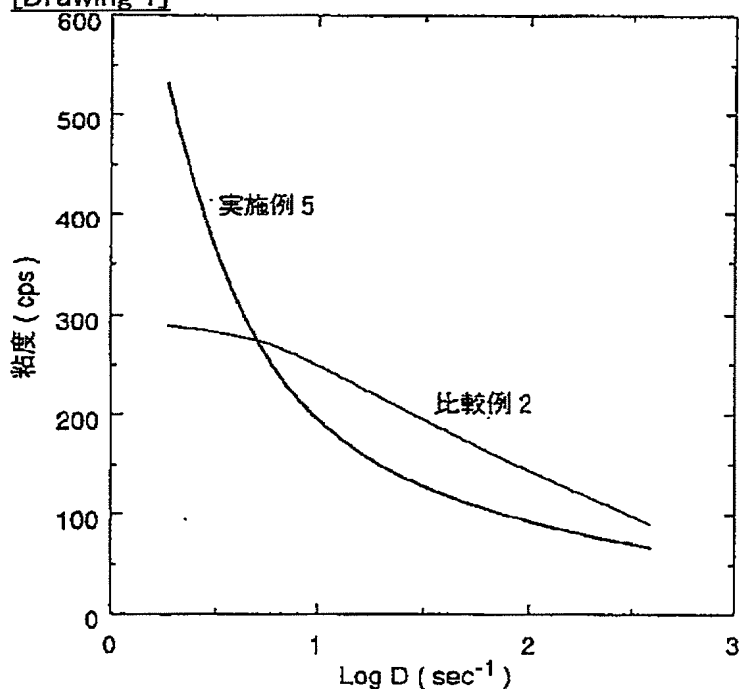
3. In the drawings, any words are not translated.

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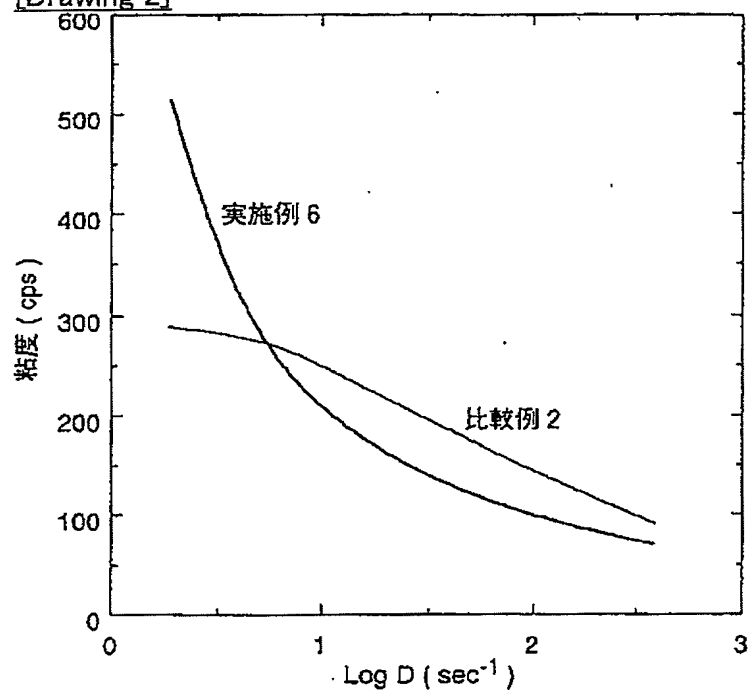
DRAWINGS

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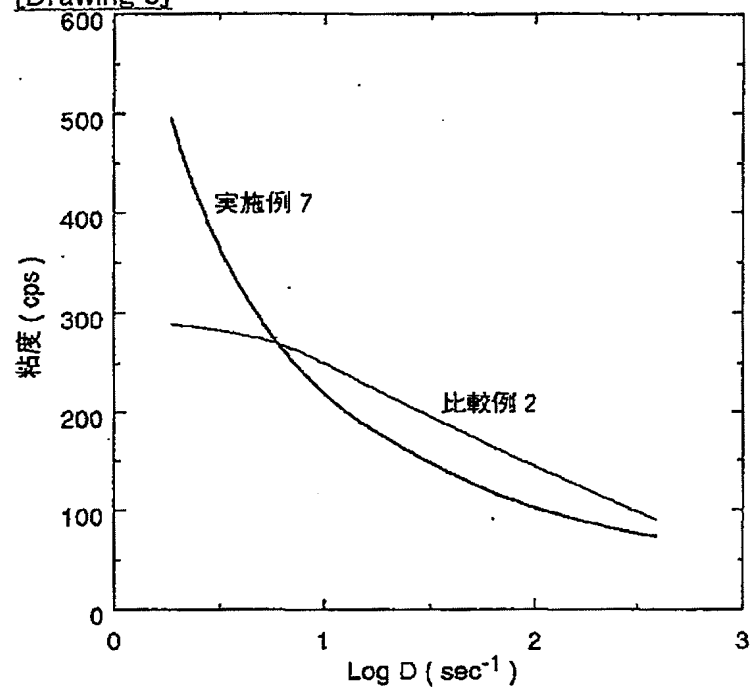
[Drawing 1]



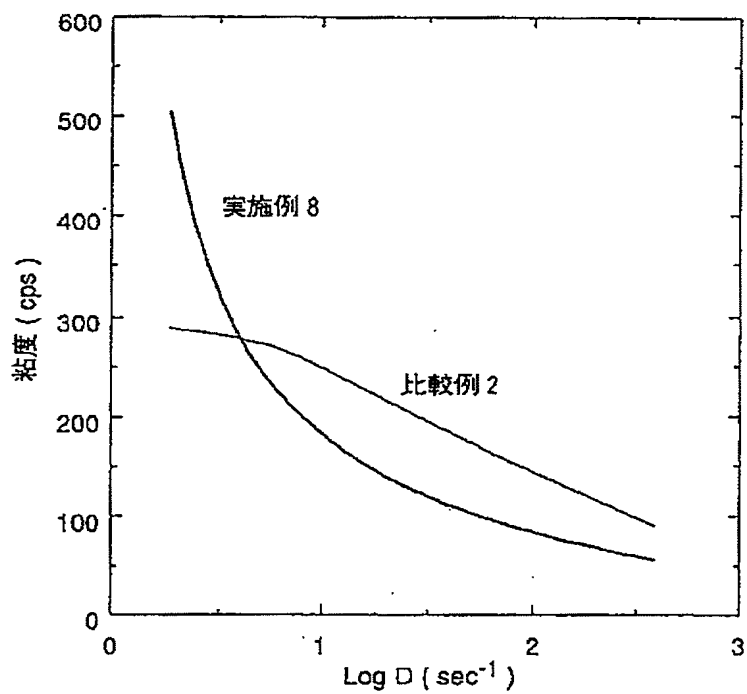
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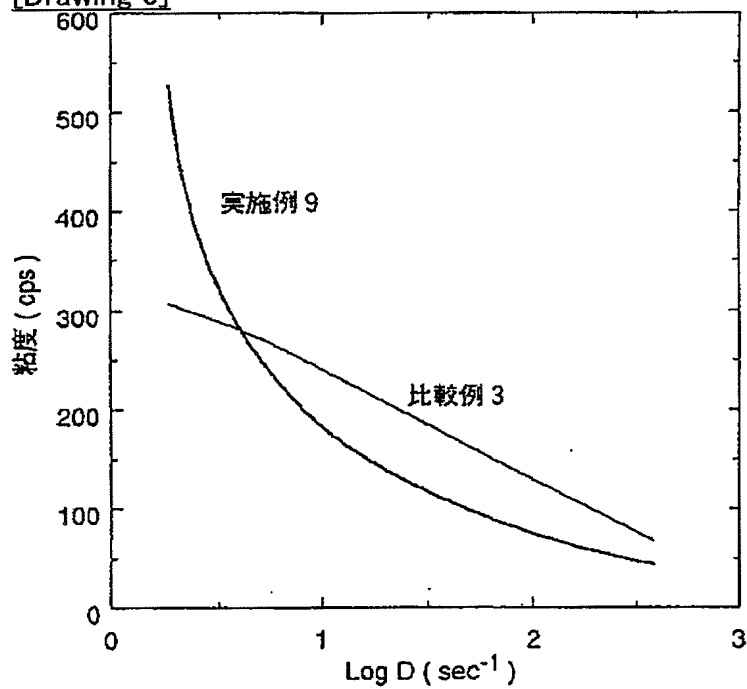
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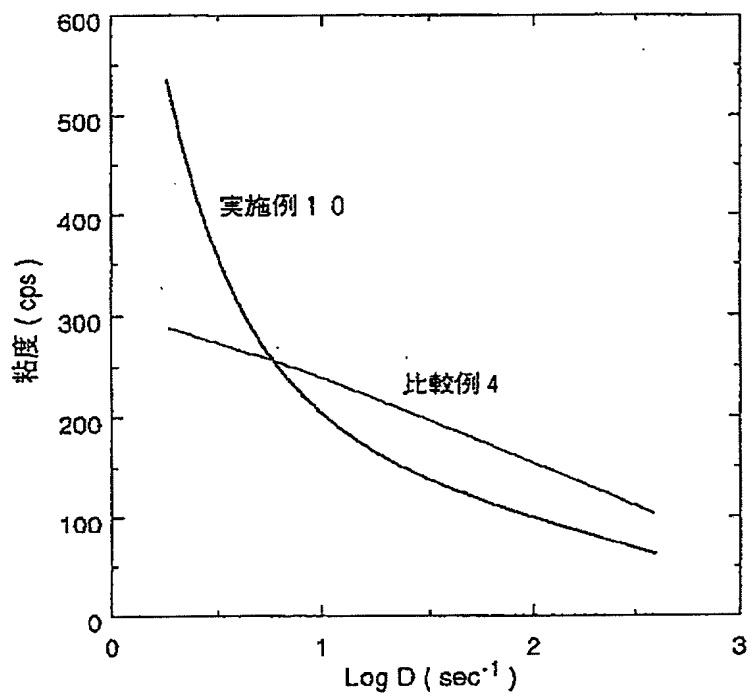
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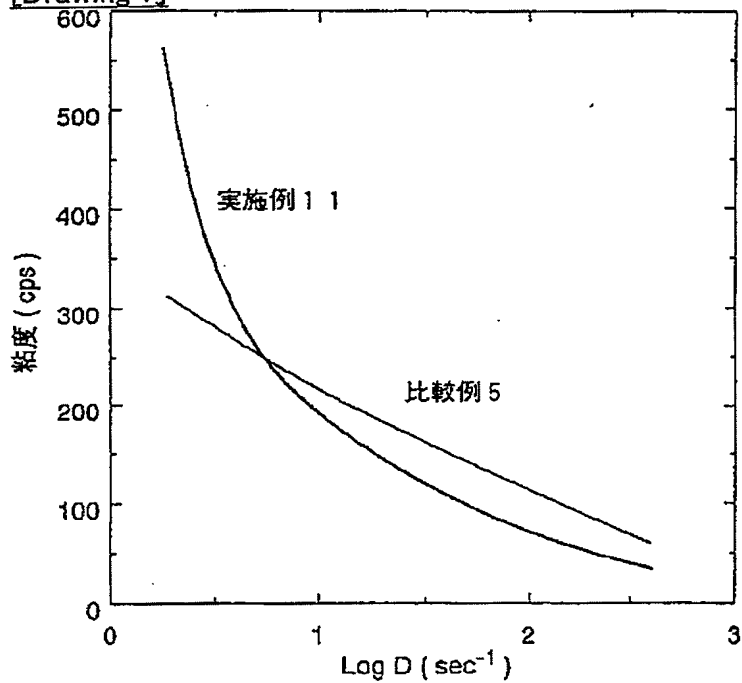
[Drawing 5]



[Drawing 6]



[Drawing 7]



[Translation done.]